Amorphous AlPO$_4$ as Catalyst Support

3. CO FTIR Study of AlPO$_4$ Impregnated with Chromium

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CO FTIR spectra of chromium/AlPO$_4$ samples give IR bands at 2192 (strong), 2212 (weak), and 2207 (weak) cm^{-1} at room temperature and after oxidation (O$_2$) and reduction (CO) at 500°C. After oxidation at 800°C and reduction at 350°C the main CO band at 2192 cm^{-1} decreases in intensity at low temperature by 20% and several groups of new CO bands at lower wavenumbers are observed [(i) 2124 and 2071 cm^{-1}; (ii) 2153, 2095, and 2034 cm^{-1}; (iii) 2121, 2109, and 2051 cm^{-1}]. These bands are interpreted as due to CO ligands bridging two chromium(II) ions of dinuclear chromium surface compounds bonded to the AlPO$_4$ surface through P–O– groups. The ratio of dinuclear chromium(II) surface species to mononuclear ones is estimated from the decrease of the band around 2185 and 2192 cm^{-1}, respectively (on cooling to low temperatures), as 3 for silica gel and 0.25 for AlPO$_4$. A weak CO band at 2202 cm^{-1} on chromium(III)/AlPO$_4$ samples is interpreted as caused by CO adsorbed on a chromium(III) surface species attached to AlPO$_4$ by Al–O– and P–O– groups. Converting this chromium(III) surface species to the chromium(II) one by oxidation at 800°C and reduction at 350°C gives two new CO bands at 2177 and 2167 cm^{-1} in addition to the one at 2192 cm^{-1}. On the basis of an increase in the ratio of the integrated absorbance of the PO–H and AlO–H groups and the opposite shift compared with CO bands on chromium(II)/silica gel samples, these IR bands are assigned to CO adsorbed on chromium(II) surface species attached to the AlPO$_4$ by Al–O– groups.   © 1991 Academic Press, Inc.

INTRODUCTION

In Part 2 (*1*) we summarized the reasons for our interest in amorphous aluminum phosphates as supports and dealt with the characterization of samples of these materials. The present paper deals with FTIR spectroscopic investigations of CO adsorbed on coordinately unsaturated chromium ions on these supports.

EXPERIMENTAL

The experimental conditions have been described in Part 2 (*1*), to which reference should be made for sample nomenclature. The conditions for the oxidation with O$_2$ and for the reduction with CO are the same as those used for the Phillips catalyst with sil-

ica gel as the support. For comparing the influence of these two supports on the chromium surface species, this approach is the most promising one. The authors are aware of the somewhat lower activation temperatures used for optimized chromium/AlPO$_4$ catalysts (*2*).

RESULTS

Figure 1 shows the FTIR spectra of CO adsorbed on sample **IA** after oxidation with oxygen at 500°C and the reduction with CO at the same temperature. At room temperature and 100 Pa CO one slightly asymmetric band is observed at 2192.5 cm^{-1} (spectrum 1), which increases in intensity and shifts slightly to 2190.1 cm^{-1} with 10 kPa CO at room temperature (spectrum 2). On cooling to −85°C (100 Pa CO) the intensity increases further (CO IR band at 2192.0 cm^{-1},

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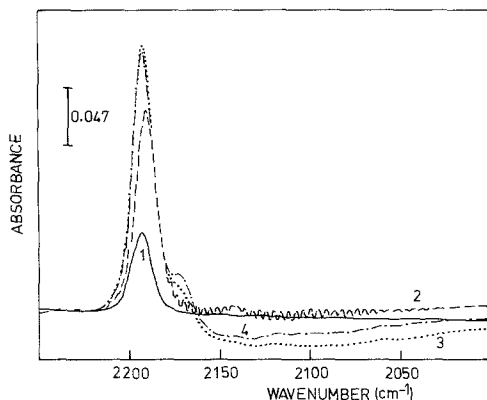[1] To whom correspondence should be addressed.

FIG. 1. FT IR spectra of CO adsorbed on chromium/ AlPO$_4$ sample **IA** after oxidation at 500°C with O$_2$ and reduction at 500°C with CO. Spectrum 1 was recorded at room temperature and 1 Pa CO, spectrum 2 at room temperature and 10 kPa CO, spectrum 3 at −85°C and 100 Pa CO, and spectrum 4 at −115°C and 100 Pa CO.

FIG. 2. FT IR spectra of CO adsorbed on chromium/ AlPO$_4$ sample **IA** after oxidation at 500°C with O$_2$ and reduction at 350°C with CO. Spectrum notation is as in Fig. 1.

spectrum 3) and a shoulder is observed at 2170.5 cm^{-1}. On further cooling to −115°C (100 Pa CO) this shoulder increases further still (spectrum 4). The latter band is due to CO weakly adsorbed on phosphorus surface hydroxyl groups (*1*). All other samples investigated, for instance **IIIC,** showed similar CO IR spectra for the same oxidation/ reduction temperatures, and are therefore not shown here.

Using the same oxidation temperature, but a lower reduction temperature of 350°C as before, introduces some changes in the FTIR spectra of CO adsorbed on chromium (Fig. 2, again sample **IA**). The band between 2191.5 (spectrum 2) and 2194.5 cm^{-1} (spectrum 3) is now broader and the shoulder at 2206.2 cm^{-1} is clearly noticeable. More important are the two new bands in the low-temperature spectrum 3 at 2124.0 and 2071.2 cm^{-1} with several weak shoulders.

For Fig. 3 again the sample **IA** has been used, but this time after an oxidation at 800°C and a reduction at 350°C. At room temperature and 10 kPa CO one band at 2192.5 cm^{-1} with a shoulder at 2206.2 cm^{-1} is observed in spectrum 1. On cooling to −85°C the band at 2192.5 cm^{-1} decreased in intensity by some 20% and 10 new CO
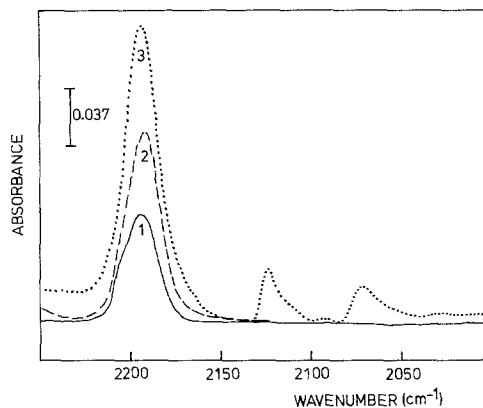
bands (or shoulders) are noticed in spectrum 2 at 2213.6, 2170.5, 2154.4, 2140.7, 2122.6, 2107.9, 2096.6, 2077.1, 2049.2, and 2036.0 cm^{-1}. On cooling to −115°C (spectrum 3) the bands at 2154.4, 2095.5, and 2036.0 cm^{-1} decreased and the bands at 2169.5, 2122.6, 2107.9, and 2049.8 cm^{-1} increased.

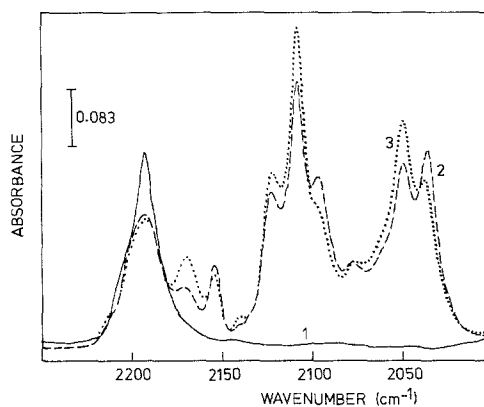This remarkable change between spectra 2 and 3 in Fig. 3 is demonstrated well in the

FIG. 3. FT IR spectra of CO adsorbed on chromium/ AlPO$_4$ sample **IA** after oxidation at 800°C with O$_2$ and reduction at 350°C with CO. Spectrum 1 was recorded at room temperature and 10 kPa CO, spectrum 2 at −85°C, and spectrum 3 at −115°C.
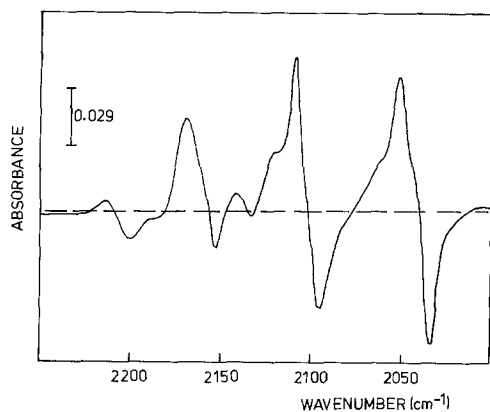
FIG. 4. Difference spectrum of CO adsorbed on chromium/AlPO$_4$ sample **IA** at different low temperatures (spectrum 3 minus spectrum 2 from Fig. 3).

FIG. 6. FT IR spectra of CO adsorbed on chromium/AlPO$_4$ sample **IIB** after oxidation at 800°C with O$_2$ and reduction at 350°C with CO. Spectrum 1 was recorded at room temperature and 1 Pa CO, spectrum 2 at room temperature and 10 kPa, spectrum 3 at −50°C and 1 kPa CO, and spectrum 4 at −115°C and 100 Pa CO.

difference spectrum in Fig. 4 (spectrum 3 minus spectrum 2 from Fig. 3). Positive CO bands are at 2213.6, 2168.5, 2140.7, 2120.6, 2108.9, and 2051.1 cm^{-1} and negative bands at 2199.9, 2152.4, 2095.2, and 2034.0 cm^{-1}. Using a reduction temperature of 250°C gave essentially the same results, although the intensity of the bands was three times weaker.

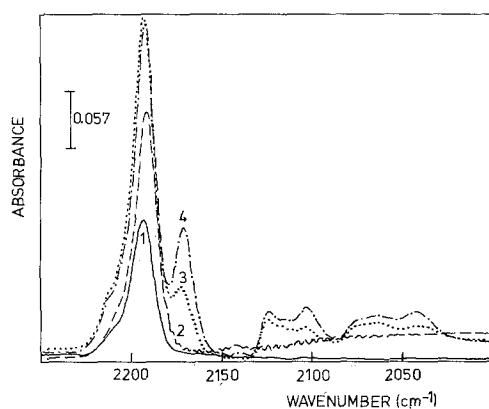Figure 5 shows spectra of sample **IA** after oxidation with O$_2$ at 800°C, reduction at

350°C, and subsequent evacuation at 700°C for 30 min. This treatment removed nearly all CO bands below 2160 cm^{-1}. On cooling (spectrum 3 and 4), the band at 2190 cm^{-1} does not decrease and only weak bands at 2123.5, 2102.5, 2073.6, 2062.9, and 2042.3 cm^{-1} are observed. In the difference spectrum (spectrum 4 minus spectrum 3 from Fig. 5, not shown) a negative band at 2195.5 cm^{-1} and positive bands at 2187.1, 2169.5, 2138.7, 2123.5, 2102.0, and 2042.8 cm^{-1} are found. This means that a chromium surface species, which adsorbs terminal CO with an IR band at 2195.5 cm^{-1} at −85°C, exchanges these with bridging CO ligands to some extent on cooling to −115°C.

FIG. 5. FT IR spectra of CO adsorbed on chromium/AlPO$_4$ sample **IA** after oxidation at 800°C with O$_2$ and reduction at 350°C with CO. The sample was heated furthermore at 700°C for 30 min under vacuum. Spectrum notation is as in Fig.1.
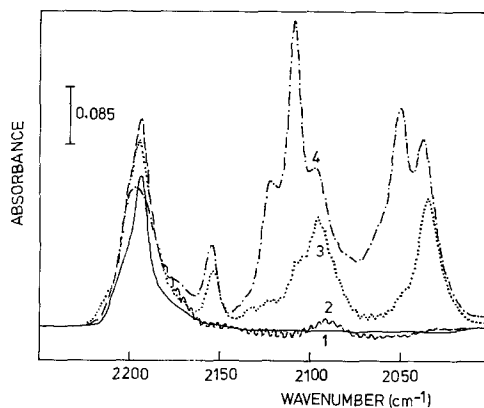
The main question now is which of the many bands belong to the same surface CO/chromium species. From Fig. 2 one surface species with two bands at 2124.0 and 2071.2 cm^{-1} and from Fig. 4 two more can be identified with bands at 2152.4, 2095.2, and 2034.0 cm^{-1} and 2199.9 (negative), (2140.7), 2120.6, 2108.9, and 2051.1 cm^{-1}. In Fig. 6, spectrum 3, it is clearly seen that the CO/chromium species with bands at 2153.9, 2095.7, and 2034.0 cm^{-1} is connected to a decreasing band at 2193.5 cm^{-1} and that the
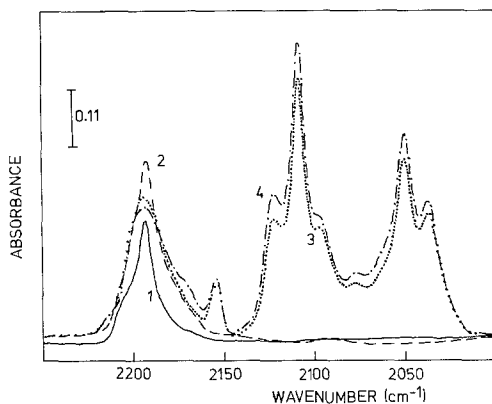
FIG. 7. FT IR spectra of CO adsorbed on chromium/ AlPO$_4$ sample **IIIC** after oxidation at 800°C with O$_2$ and reduction at 350°C with CO. Spectrum notation is as in Fig. 1.

FIG. 9. FT IR spectra of CO adsorbed on chromium/ AlPO$_4$ sample **IIB** after oxidation at 800°C with O$_2$ and reduction at 350°C with CO. The sample was then oxidized by H$_2$O/O$_2$ at room temperature and heated to 800°C for 15 min under vacuum. Spectrum notation is as in Fig. 1.

intensity of the three bands is increasing with decreasing wavenumber. The bands with higher and lower wavenumbers are nearly symmetrically shifted from the band in between, i.e., 58.2 and 61.7 cm^{-1}. A CO band at 2089.3 cm^{-1} is seen in spectrum 2, Fig. 6, and might be a precursor CO/chromium complex to the one with the three bands.

From Figs. 7 and 8 using sample **IIIC**, it becomes clear that a CO/chromium species exists, showing a negative band from termi-
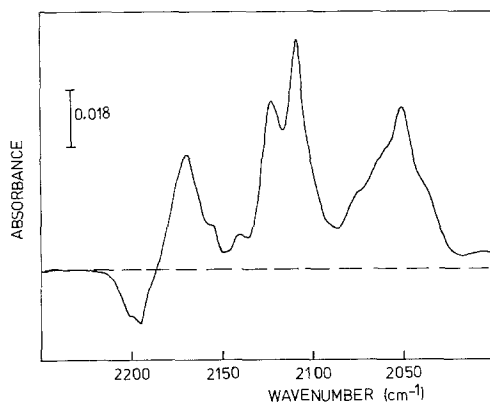
nal CO ligands at 2195.5 cm^{-1} in the difference spectrum in Fig. 8 and three positive bands at 2122.1, 2108.4, and 2050.7 cm^{-1}. A slightly different CO/chromium species was seen on a **IIIB** sample with bands at 2192.0 (negative), 2122.6, 2099.1, and 2057.0 cm^{-1}.

Figure 9 shows CO FTIR spectra of chromium(III) on a **IIB** sample. To form this chromium(III) surface compound we first prepared a chromium(II) sample by oxidation/reduction at 850 and 350°C and oxidized with H$_2$O/O$_2$ at room temperature (*3*). The water was removed by evacuation, and a sample disk pressed and heated in the IR cell to 800°C under vacuum. In spectrum 1 two bands at 2211 and 2193.2 cm^{-1} are noticed at room temperature and 100 Pa CO. Both are due to relatively strong CO complexes. At room temperature and 10 kPa CO only the band at 2193.2 cm^{-1} grows in intensity. After cooling to low temperatures (spectra 3 and 4 in Fig. 9) a new band at 2202 cm^{-1} of weakly bonded CO appears, while the band at 2194.4 cm^{-1} shows only a minor increase and that from CO adsorbed on phosphorus surface groups at 2171.0 cm^{-1} is increasing strongly.

After application of the usual oxidation/ reduction procedure at 800 and 350°C to the

FIG. 8. Difference spectrum of CO adsorbed on chromium/AlPO$_4$ sample **IIIC** at different low temperatures (*spectrum 3 minus spectrum 2 from Fig. 7*).
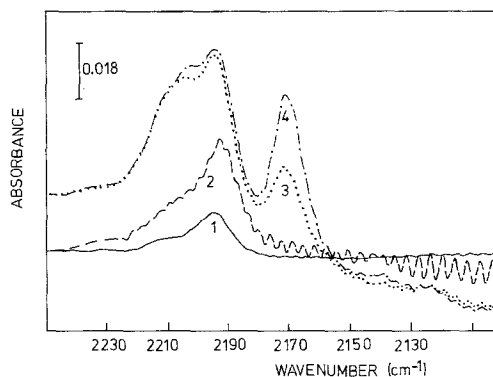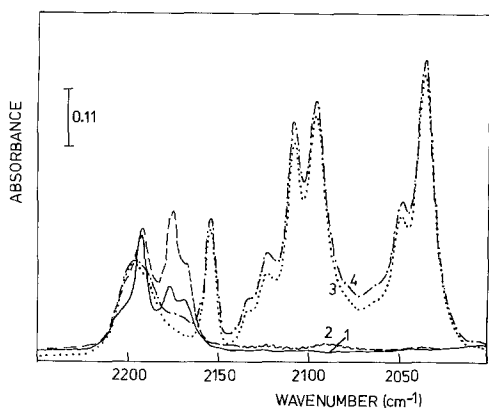
FIG. 10. FT IR spectra of CO adsorbed on chromium/AlPO₄ sample **IIA** prepared as for the chromium(III) sample in Fig. 9. Thereafter the sample was oxidized at 800°C with O₂ and reduced at 350°C by CO. Spectrum notation is as in Fig. 1.

chromium(III) sample disk, two new CO bands at 2177.1 and 2168.9 to 2166.0 cm⁻¹ appeared. For the spectra in Fig. 10 sample **IIA** has been used instead of **IIB** as in Fig. 9. As one can see from spectra 1 and 2, these new bands are present in the room temperature spectra with 10 kPa and 100 Pa CO. They vanish at low temperature (spectrum 3) and are therefore quite different from those of CO adsorbed on phosphorus surface hydroxyl groups, which are only stable at low temperatures and appear in spectrum 4 in Fig. 10. A more detailed picture of the bands between 2210 and 2160 cm⁻¹ is given in Fig. 11. One can clearly see four bands at 2206.7, 2192.6, 2177.1, and 2168.9 cm⁻¹. The latter band is shifted to 2166.0 cm⁻¹ after evacuation at elevated temperatures and the adsorbed CO giving this band is bonded nearly as strongly as the one with the band at 2206.7 cm⁻¹. On the other hand the adsorbed CO with the band at 2177.1 cm⁻¹ is completely removed by evacuation and that with the band at 2192.6 cm⁻¹ nearly so. One should also notice that the band at 2177.1 cm⁻¹ is decreasing much faster with decreasing CO pressure at room temperature than the band at 2192.0 cm⁻¹, as can be seen by comparing spectra 2 and 3 in Fig. 10.

The ratio of the integrated absorbance for PO–H and AlO–H groups [see Fig. 11 in Part 2 (1)] decreases from the unimpregnated to impregnated chromium(II) sample, from 3.34 to 3.07. This means that the number of POH groups has decreased more than the number of AlOH groups. This is additional evidence that chromium(II) is bonded to the surface of amorphous AlPO₄ via PO–groups. Chromium(III) and chromium(II) samples (the latter prepared from chromium(III)) show values of 5.19 and 4.96 for this ratio of different surface hydroxyl groups. This means that the number of surface AlOH groups decreased more in relation to the number surface POH groups in the latter two cases. In both cases the AlO–H IR band at 3768.5 cm⁻¹ was no longer present. This is evidence that for the formation of chromium(III) surface compounds on AlPO₄ also AlO– groups are used.

It was not possible to identify CO bands, connected to the bands at 2177 and 2166 cm⁻¹, at wavenumbers lower than 2160 cm⁻¹ in difference spectra from low-temperature spectra. That such CO bands are formed is concluded from the removal of the bands at 2177 and 2166 cm⁻¹.

Table 1 gives a summary of the CO bands from different chromium surface species on
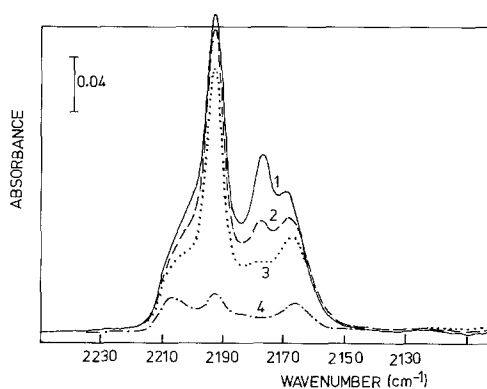

FIG. 11. FT IR spectra of CO adsorbed on chromium/AlPO₄ sample **IIA** prepared as the sample used for Fig. 10. Spectrum 1 was recorded after evacuation (1 Pa CO) at room temperature, spectrum 2 at 50°C, spectrum 3 at 100°C, and spectrum 4 at 200°C.

TABLE 1

Different CO/Chromium Complexes Deduced from the CO FTIR Spectra

Sample and preparation conditions	CO IR bands (cm^{-1}) at wavenumbers beyond 2160 cm^{-1}	CO IR bands (cm^{-1}) at wavenumbers below 2160 cm^{-1}		
IA 500/500	2192	—		
IA 500/350	2206.2/2192(−)	2124.0,	2071.2	
IA 800/350	2193.5(−)	2152.4,	2095.2,	2034.0
IIIC 800/350	2199.9(−)	2120.6,	2108.9,	2051.1
IA 800/350/700(Cr^{2+})	2195.5(−)	2123.5,	2102.0,	2042.8
IIIB 800/350	2192.0(−)	2122.6,	2099.1,	2057.0
IIB 800/350/700(Cr^{3+})	2211,*2202*,2194	—		
IIA 800/350/700–800/350	2207,2193(−),*2177*(−),*2169*(1)	?^{a}		

Note. The minus sign in parentheses means that this IR band decreases or is removed at temperatures below room temperature.

^{a} For significance, see text.

amorphous AlPO$_4$ and shows that at least eight different species can be identified on this support. In Table 1 not all CO bands for each sample are listed, but rather those that define additional chromium surface species observed especially well on these samples. The question mark in the last line of the table indicates that low wavenumber bands corresponding to the bands at 2177 and 2169 cm^{-1} have not been observed, although there are reasons why they should exist (see Discussion).

DISCUSSION

Six different chromium surface species can be identified on silica gel by using the CO FTIR technique (*4*). These are mono- and dinuclear chromium(II)-A with CO IR bands at 2185 cm^{-1} and 2179, 2185, 2120, 2100, 2035 cm^{-1}, respectively (*5–8*). The bands at 2179 and 2185 cm^{-1} decrease on cooling to low temperatures by some 75%, while the new three bands at 2120, 2100, and 2035 cm^{-1} appear. The chromium(II)-A species is highly coordinatively unsaturated with only two oxygen ligands at the chromium ion and the three new CO IR bands at low temperature below 2143 cm^{-1}, the CO stretching vibration of CO gas, are interpreted as due to three CO ligands bridging two

chromium ions (*5, 6*). The chromium(II)-A surface species are formed on silica gel after oxidation/reduction at 800 and 350°C. The chromium(II)-B species is formed after oxidation/reduction at 500 and 500°C (*9, 10*) and shows only the CO band at 2190 cm^{-1}, which is assigned to CO adsorbed on a mononuclear chromium(II) surface compound with one extra oxygen ligand from a surface silanol group. A third chromium(II) surface species can be prepared from the chromium(II)-A species by heating the sample to 700°C under vacuum and this dinuclear chromium(II)-C species has a CO band at 2190 cm^{-1}, which decreases on cooling, while new bands appear at 2120, 2100, and 2045 cm^{-1} (*5*). On cooling to lower temperatures, both mono- and dinuclear chromium(III) surface species give only one CO band at 2200 cm^{-1} (*5*).

Amorphous AlPO$_4$ is structurally very similar to amorphous silica gel, because both are built with tetrahedral units, either SiO$_4$ or AlO$_4$ and PO$_4$ ones. This simple statement, however, does not include all the results observed in Part 2 (*1*) (i.e., several aluminum surface hydroxyl groups) and must consequently be modified. In view of the aluminum surface hydroxyl groups at 3768.5 and 3743.5 cm^{-1} it was concluded

that not only tetrahedral AlO_4 units but also five (and six)-coordinated AlO_x units exist on the $AlPO_4$ surface.

The interpretation of the CO IR bands will be based on a simplified bonding model where shifts to higher wavenumbers (from the CO stretching vibration in CO gas at 2143 cm⁻¹) are interpreted as drawing electron density from the CO ligands and shifts to lower wavenumbers as pushing electrons into the CO ligands (10). Because the more acidic phosphorus surface hydroxyl groups will react much easier than the aluminum ones (11) and because of the decreased electron density at the oxygen from P–O– surface groups (1, 11), all bands between 2200 and 2190 cm⁻¹ are assigned to terminal CO adsorbed at chromium(II) surface compounds bonded to the $AlPO_4$ via P–O– groups.

Consequently the two bands at 2177 and 2167 cm⁻¹ are assigned to terminal CO adsorbed at chromium(II) surface compounds bonded to the $AlPO_4$ via Al–O– groups. In view of the facts that the latter chromium surface species is formed with the chromium(III) surface species as an intermediate and the same position of the CO band adsorbed on chromium(III) on $AlPO_4$ and on silica gel at 2200 cm⁻¹ (5), we conclude that the chromium(III) is bonded to the $AlPO_4$ by P–O– and Al–O– groups. These conclusions are supported by the remarkable increase of the ratio of integrated intensity from PO–H and AlO–H surface groups observed above for chromium(II) and chromium(III) samples (from 3.07 to 5.19). This means that the AlO–H surface groups are decreasing in number compared to PO–H surface groups and that AlO–H groups should be involved in the formation of the chromium(III) and the special chromium(II) surface species with bands of adsorbed CO at 2177 and 2166 cm⁻¹.

When the samples are cooled to low temperature, the CO band around 2192 cm⁻¹ decreases by some 20% on chromium(II) on $AlPO_4$, while the band around 2185 cm⁻¹ decreases on chromium(II) on silica gel by

some 75% (5). Because this decrease is inverse to the appearance of the low-temperature bands from bridging CO ligands, this decrease is interpreted as a measure of the content of dinuclear chromium(II) surface species. In other words the ratio of dinuclear chromium(II) surface species to the mononuclear one is roughly 3 for silica gel and 0.25 for amorphous aluminum phosphate. These ratios can be correlated to the observation that addition of triethylborane to the chromium catalyst has little effect on the polymerization activity for chromium/silica gel catalysts, while it enhances the activity in the case of chromium/AlPO₄ catalyst by a factor of 5 (2). One should add that one of the authors has proposed that only dinuclear chromium(II) surface species are catalytically active for the polymerization (without extra help by alkylating agents, i.e., triethylborane). Because the two CO bands at 2177 and 2167 cm⁻¹ are removed completely at low temperatures, it is concluded that chromium(II) attached to the $AlPO_4$ by AlO– groups exists only as dinuclear surface species.

The bands at low temperatures below 2160 cm⁻¹ are interpreted again as due to bridging CO ligands on dinuclear chromium(II) surface species. The three bands between 2120–2124, 2099–2109, and 2043–2057 cm⁻¹ (see Table 1) are similar to those found for the chromium(II)-A and chromium(II)-C species on silica gel. In contrast to the other species with CO bands at 2152, 2095, and 2034 cm⁻¹, where the two outer bands have similar distances from the middle one (57 and 61 cm⁻¹), this is not the case for the other three chromium(II) surface species with bridging CO ligands (20 and 50 cm⁻¹). We think that the existence of several dinuclear chromium(II) surface species on $AlPO_4$ is caused by the more irregular surface structure due to the existence of four- and five (and six)-coordinated AlO_x units and that oxygen atoms from the support surface may be weak additional ligands at the chromium ions.

One might expect that when the bands

from terminal CO adsorbed on chromium(II) surface compounds are shifted to higher wavenumbers, the corresponding bands from bridging CO should be shifted in the same direction. This is indeed observed for the chromium(II)-C species on silica gel compared to the chromium(II)-A one (2178 to 2190 cm^{-1} and (2120, 2100) 2035 to 2050 cm^{-1} (5)). This effect is also observed with chromium on AlPO$_4$ for one group of chromium(II) surface compounds as reported above.

A chromium(II) surface compound on AlPO$_4$ similar to the chromium(II)-B or chromium(II)-C species on silica gel (one extra oxygen ligand from surface silanol or surface siloxane groups) is assigned to the band from terminal CO at 2206 cm^{-1} in Figs. 2 and 11 and to the CO IR bands at 2124 and 2071 cm^{-1} from bridging CO in Figs. 2 and 5. However, in contrast to chromium on silica gel, where the chromium(II)-B and chromium(II)-C species can be produced in relatively high yields under suitable conditions, only small concentrations of similar chromium(II) surface species are observed on AlPO$_4$.

One can conclude that AlPO$_4$ is a spectroscopically and structurally more complicated support than silica gel, but which, similarly to silica gel, has different chromium surface species depending on the pretreatment conditions. With AlPO$_4$ supports having different surface areas and pore volumes similar surface compounds are found, although the surface area and pore volume have great influence on the performance of the catalyst in the industrial polymerization. This effect is already known from silica gel as the support for the traditional Phillips catalyst.

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